



Technical note

Porous platinum electrodes derived from the reduction of sputtered platinum dioxide films

L. MAYA¹, G.M. BROWN¹ and T. THUNDAT²

¹Chemical and Analytical Sciences Division; and

²Life Sciences Division, Oak Ridge National Laboratory Oak, Ridge, TN 37831, USA

Received 28 September 1998; accepted in revised form 19 January 1999

Key words: platinum electrodes, platinum oxide, porous electrodes, sputtering

1. Introduction

The present study was undertaken to establish whether highly porous platinum dioxide films deposited by reactive sputtering of platinum in an oxygen plasma could serve as precursor to high specific surface area electrodes of platinum. The chemistry underlying such process is quite simple and has as its precedent the wide use of platinum dioxide, also known as Adams' catalyst, as the precursor of finely divided metallic platinum in the hydrogenation of organic compounds [1]. Metallic electrodes with high specific surface areas may be advantageously incorporated in batteries, fuel cells and sensors [2–4] because of considerations such as efficiency and the ultimate size of the device. High surface area electrodes may be prepared by controlling electrodeposition parameters [5] or as described by Attard et al. [2] through the use of the ordered pore structure of a lyotropic liquid crystalline phase. Additional methods include thermal decomposition of a precursor [6] or through sputtering [7]. The latter method provides a great deal of flexibility since complex targets may be sputtered and also the chemistry of the process may be modified through the participation of a reactive plasma medium [8].

2. Experimental details

Platinum dioxide films were prepared by reactive sputtering using a 40 vol % oxygen in argon in a parallel-plate d.c. glow discharge as previously described [9]. In this study the films, 2–4 μm thick, were deposited on gold foil discs 6.35 mm in diameter. The platinum oxide was characterized by chemical analysis, infrared spectroscopy and X-ray diffraction. Reduction to platinum was conducted by exposure, at room temperature, to a

stream of 4 vol % hydrogen in argon. Alternatively, the oxide may be reduced electrochemically. This was done for a few specimens prior to conducting the cyclic voltammetry runs by holding the working PtO_2 coated electrode, at -0.3 V vs SCE for a few minutes. Platinum films were also prepared, for comparison purposes, by directly sputtering in pure argon plasma. Film densities were derived from the area and gain in weight of the coated substrates followed by thickness determination with a surface profiler. The microstructure of the films was examined by atomic force microscopy using a Nanoscope III in the tapping mode. Cyclic voltammetry was conducted on the films after mounting the foil disc on a Kel-F holder machined from a 9.5 mm diameter rod with an inner channel for electrical connection and fitted with a drilled cap on one end to hold the foil. The coated side of the foil was exposed to electrolyte and electrical contact was made from the back of the foil. Exposure of the foil to electrolyte was limited by a sealing gasket to an area 1.4 mm in diameter. The electrode containing the coated foil was sealed by means of an O-ring into a two-compartment electrochemical cell along with a calomel reference electrode. A platinum coil was used as counter electrode in the second compartment. The electrolyte was prepared from Ultrex high purity H_2SO_4 diluted to 0.5 M. The system was sparged with helium.

3. Results and discussion

3.1. X-ray characterization

Films of the precursor oxide and the hydrogen-reduced product were examined. The corresponding diffraction patterns are shown in Figures 1 and 2, respectively. The pattern of the oxide is that of $\alpha\text{-PtO}_2$ which is a

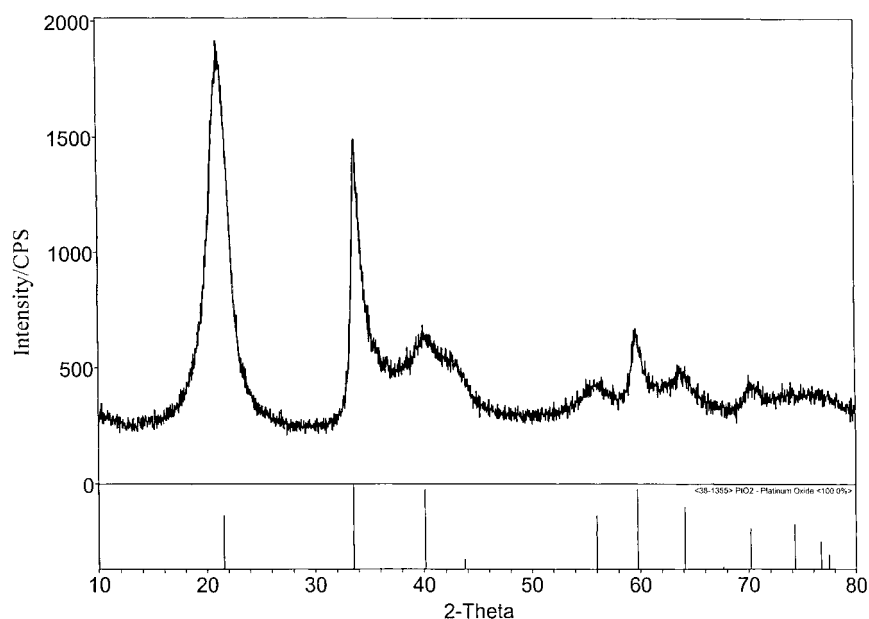


Fig. 1. X-ray diffraction pattern of sputtered α -PtO₂ film. Inset: standard pattern from the International Center for Diffraction Data.

hexagonal crystalline phase with a structure similar to that of layered CdI₂ [10]. Also given in Figure 2 is the diffraction pattern of a platinum film sputtered with argon instead of the oxygen–argon mixture, using the same apparatus and power density. The argon-sputtered film was prepared for the purposes of comparison: namely, to demonstrate that the intermediate oxide

deposition followed by reduction was necessary, as indeed it was, in order to produce a film with a smaller crystallite size and a more porous structure. That difference is evident in the width of the corresponding diffraction lines and through the microstructural examination, to be discussed in a different section. In addition to this, visual inspection readily distinguishes the argon-

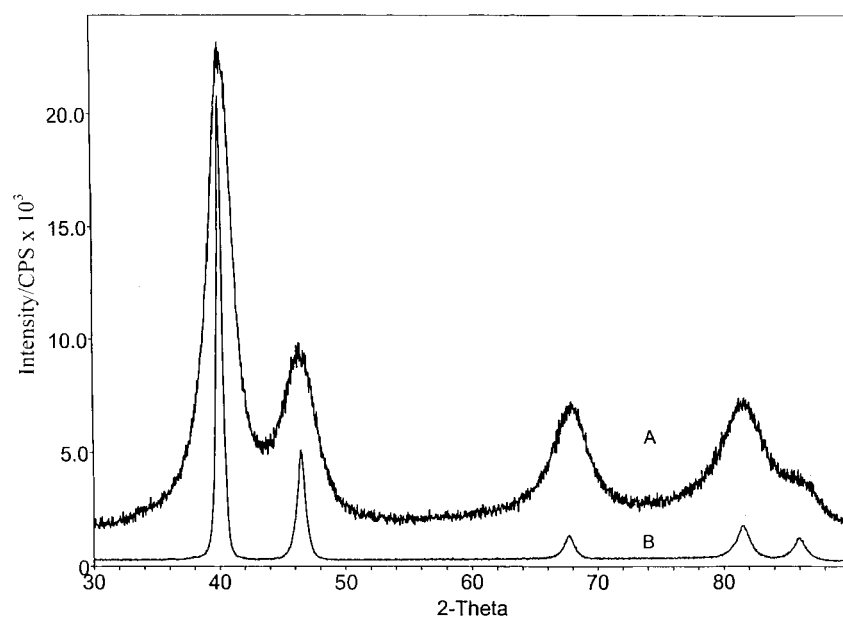


Fig. 2. X-ray diffraction pattern of A: platinum derived from the reduction of platinum dioxide, B: platinum from argon sputter of platinum foil.

sputtered film and the hydrogen-reduced film; the former is highly reflective while the latter is dark and dull in appearance because of light scattering.

3.2. Film density

The density of the precursor oxide was 2.0 g cm^{-3} , which is about 20% of the theoretical density, derived from the dimensions of the single cell parameters of the hexagonal phase. Reduction in argon–hydrogen leads to oxygen loss and compression to about 50% of the initial volume for a density of 3.4 g cm^{-3} , which is about 16% of the density of platinum metal. On the other hand, the density of the argon-sputtered films was 16.3 g cm^{-3} corresponding to about 76% of the density of platinum.

3.3. Microstructure

The microstructure of the precursor film appears as a porous disordered assembly of platelets, illustrated in Figure 3, that changes little upon reduction in hydrogen, Figure 4 and thus suggested the potential of these platinum films as high specific area electrodes. In contrast with these images; the argon sputtered film which is evidently denser, is composed of a closer assembly of round particles as seen in Figure 5. Finally,

the microstructure of an electrochemically-reduced film is shown in Figure 6 which appears as flakes of connected particles and a relatively large proportion of voids.

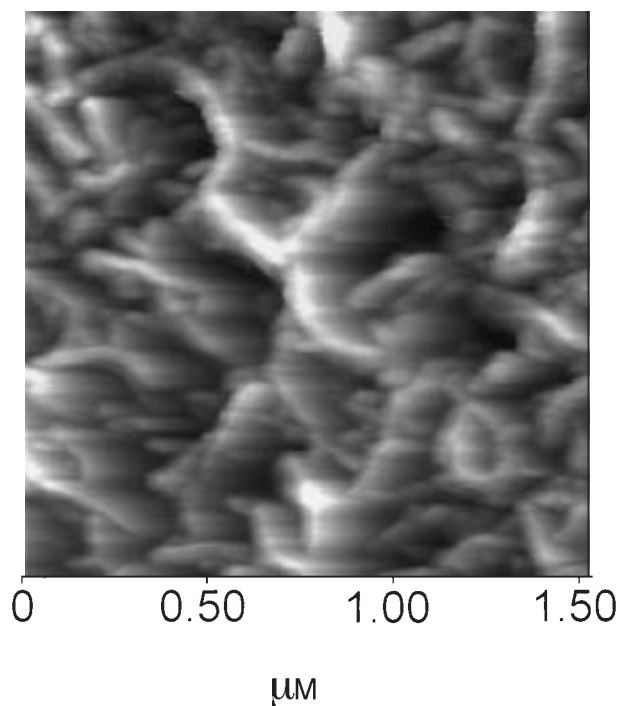


Fig. 4. Atomic force micrograph of hydrogen-reduced $\alpha\text{-PtO}_2$.

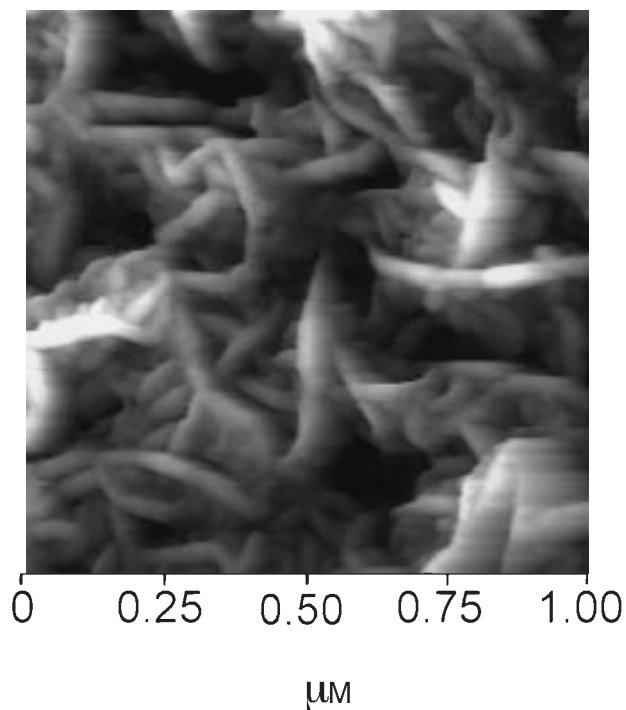


Fig. 3. Atomic force micrograph of sputtered $\alpha\text{-PtO}_2$.

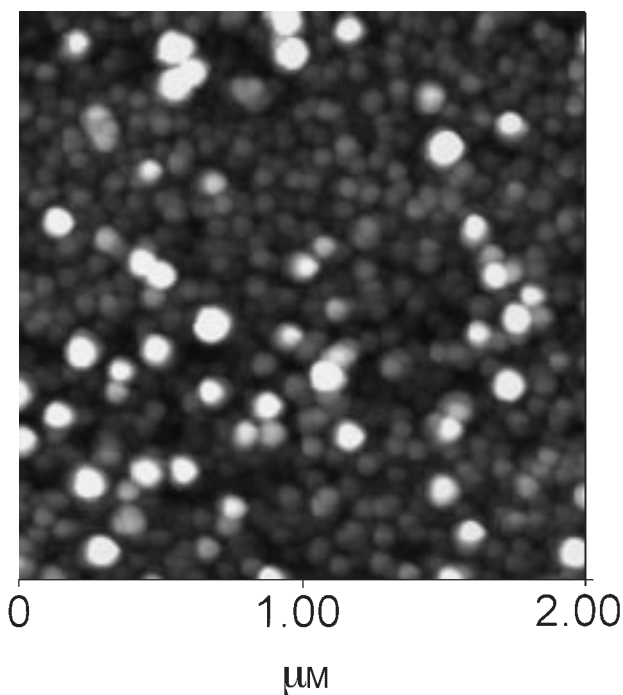


Fig. 5. Atomic force micrograph of argon-sputtered platinum film.

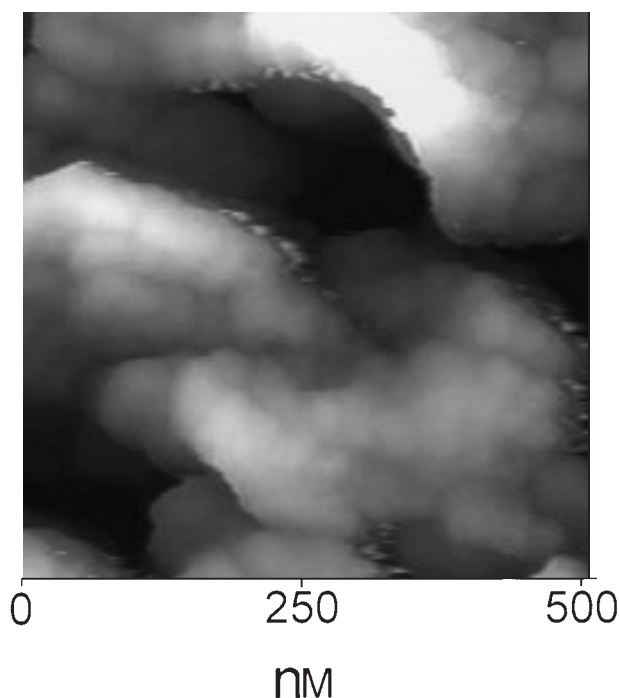


Fig. 6. Atomic force micrograph of electrochemically reduced α -PtO₂.

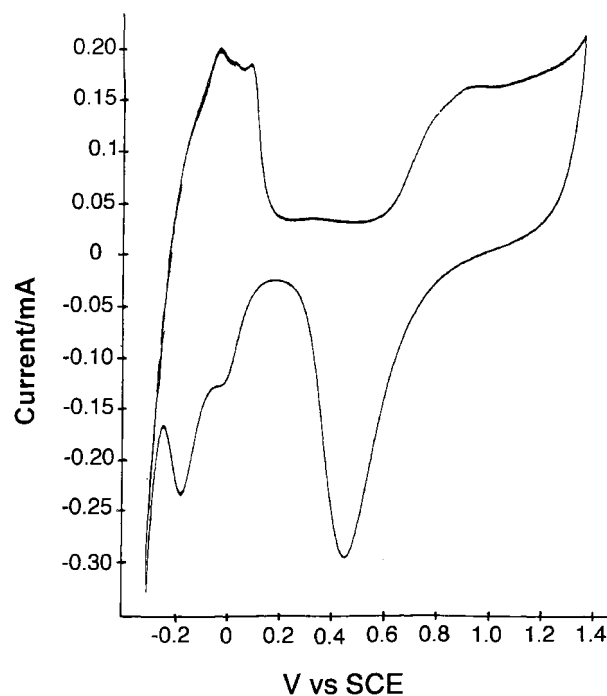


Fig. 7. Cyclic voltammogram, scanned at 0.2 V s⁻¹, of electrochemically reduced α -PtO₂.

3.4. Electrochemical behaviour

Cyclic voltammograms were recorded for all the films at scanning rates of 0.02, 0.05, 0.1 and 0.2 V s⁻¹. The typical features corresponding to electroadsorption–electrodesorption of oxygen and hydrogen adatoms on platinum [2, 11] were observed and are illustrated in Figure 7. The electroactive area for different electrodes was derived from the charge associated with hydrogen adsorption and desorption process that takes place as the electrode is cycled between 0.2 and -0.2 V vs SCE. The capacitive charge associated with those processes was excluded. The values are given in Table 1, which also includes results from [2] and, for comparison, the results of plain unpolished platinum wire.

Films A and B were initially 3 μ m thick and their platinum content 0.6 mg cm⁻² while film C was 0.7 μ m thick and the platinum content 1.1 mg cm⁻².

The electrochemical reduction of the oxide-derived film in the area exposed to the electrolyte provides a proof of principle demonstration, albeit in a macroscopic scale, of the feasibility to conduct localized generation of platinum features surrounded by oxide, which is an electrical insulator. This is illustrated by the X-ray diffraction pattern given in Figure 8 showing the presence of electrochemically generated platinum along with the oxide source outside the exposure area as well as the pattern of gold which was the substrate. This is of importance as it demonstrates the feasibility of using platinum dioxide as a medium for maskless generation

Table 1. Areas and roughness factors for different Pt specimens

Sample	Treatment	Geometric area cm ² (A-g)	Electrochemical area cm ² (A-e)	Roughness factor (A-e)/(A-g)
A	Electrochemical reduction of PtO ₂	0.015	2.25	150
B	Hydrogen reduction of PtO ₂	0.015	1.73	115
C	Argon sputter of Platinum foil	0.015	0.74	49
Pt wire	None	0.6	0.9	1.5
Ref. [2]	Pt deposition in liquid crystal medium	0.008	5.47	684

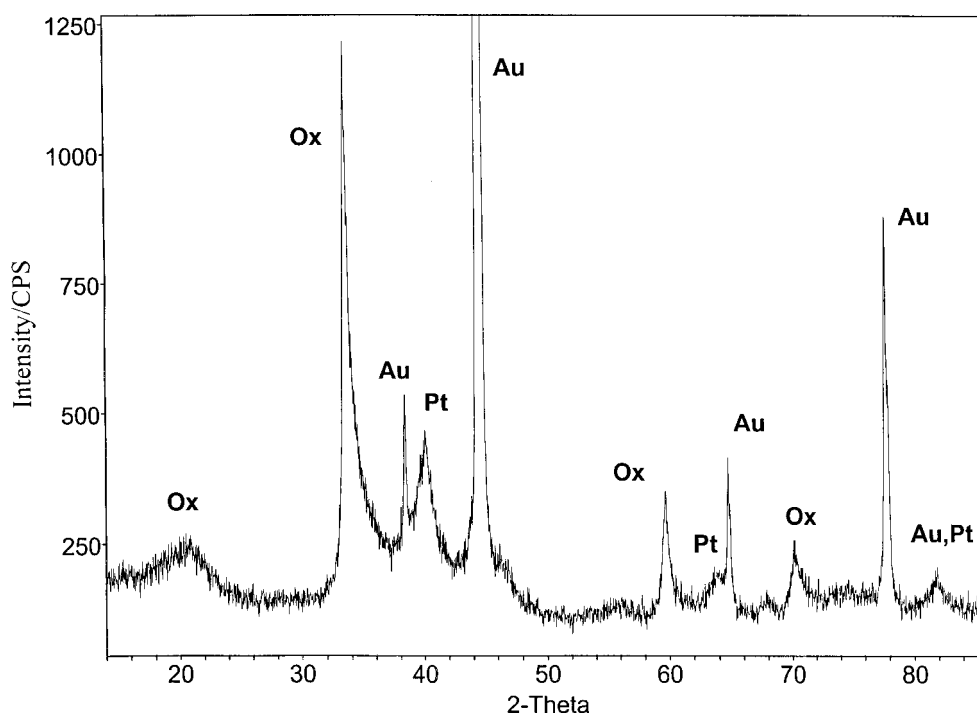


Fig. 8. X-ray diffraction pattern of gold foil coated with sputtered α -PtO₂ subjected to localized (1.6 mm area) electrochemically generated platinum. Different features due to the oxide, gold and platinum are labelled as Ox, Au, and Pt, respectively.

of microscopic metallic platinum features by means scanning tunneling microscope, STM. A system may be visualized whereby a conducting substrate, coated with platinum dioxide constitutes one electrode of an electrochemical cell and the conducting tip of a STM is used as a working electrode that is brought in close proximity to the oxide to affect reduction in a localized fashion. Precedents of such electrochemical nanofabrication are known [12]. If carried to its ultimate idealized limit it would be possible to fabricate platinum quantum dots a few nanometers in diameter. Such features may then be used as single electron devices. The microstructure of crystalline α -PtO₂ (Figure 3) does not lend itself to such use because of considerable roughness but amorphous PtO₂ films that are smoother [13] are under investigation.

4. Conclusions

Sputtered platinum dioxide films provide a convenient precursor for the generation of large specific area platinum electrodes and thus an alternative of electrochemically platinized electrodes. Reduction of the oxide is readily accomplished through exposure to hydrogen or by electrochemical means. Deposition of a platinum film directly, by sputtering platinum metal, does not

generate a microstructure as porous as that obtained through the intermediate generation of crystalline platinum dioxide. Platinum dioxide may be reduced in a localized manner to generate platinum features surrounded by the oxide precursor.

Acknowledgements

This work was sponsored by the US Department of Energy, Office of Basic Energy Sciences under contract number DE-ACOR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research. Additional support received from the Laboratory Directed Research and Development Fund.

References

1. R.L. Augustine, *Catalytic Hydrogenation*, Dekker, New York. 1965.
2. G.S. Attard, P.N. Bartlett, N.R.B. Coleman, J.M. Elliot, J.R. Owen and J.H. Wang, *Science*, **278** (1997) 838.
3. S. Ye, A.K. Vijh and L.H. Dao, *J. Electrochem. Soc.* **143** (1996) L7.
4. J. Wang and L. Angnes, *Anal. Chem.* **64** (1992) 456.
5. D. Landolt, *Proc. Electrochem. Soc.* **96-19** (1997) 160.
6. J. Melsheimer and D. Ziegler, *Thin Solid Films* **163** (1988) 301.
7. H. Tanabe and S. Fukushima, *Electrochim. Acta*, **29** (1984) 1173.
8. K. Reichelt and X. Jiang, *Thin Solid Films* **191** (1990) 91.

9. L. Maya, E.W. Hagaman, R.K. Williams, X.-D. Wang, G.D. Del Cul and J.N. Fiedor, *J. Phys. Chem. B* **102** (1998) 1951.
10. J.R. McBride, G.W. Graham, C.R. Peters and W.H. Weber, *J. Appl. Phys.* **69** (1991) 1596.
11. L. Bai, L. Gao and B.E Conway, *J. Chem. Soc. Faraday Trans.* **89** (1993) 243.
12. T. Thundat, L.A. Nagahara and S.M. Lindsay, *J. Vac. Sci. Technol. A* **8** (1990) 539.
13. L. Maya, L. Riester, T. Thundat and C. S. Yust, *J. Appl. Phys.* **84** (1998) 6382.